STUDIES IN CONJUGATED SYSTEMS:

PART I. THE SYNTHESIS OF 1-PHENYL-2,3-DIMETHYLBUTADIENE-1,3; A RE-EXAMINATION

PART II. THE ADDITION OF HYDROGEN AND OF HYDROGEN BROMIDE TO 1-PHENYL-2,3-DIMETHYLBUTADIENE-1,3

A THESIS

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BY

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CHAPTER I

INTRODUCTION

The determination of the modes of addition of addenda to conjugated systems is of considerable theoretical importance. A search of the literature reveals the fact that during the last half century a tremendous amount of experimentation has been done on this subject which has given rise to a great deal of controversy. Northrup,[1] Kharasch,[2] Sampey,[3] and Muskat[4] have reported extensive work on the modes of addition of addenda to butadiene and many of its homologues. Most of the workers agree on the theory that the orientation of the entering group in the molecule is dependent on both the nature of the molecule and the nature of the addendum.

During the past decade work with conjugated systems has been in progress in these laboratories with emphasis on the methods of preparation of these conjugated compounds and on

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[1]Herbert E. Northrup, "The Preparation and Chlorination of Butadiene, (Unpublished Master's Thesis Presented to the University of Chicago, June, 1930), p. 1.1.

[2]Kharasch and Reinmuth, J. Chem. Educ., 8, 1703 (1931).

[3]John R. Sampey, J. Chem. Educ., 4, 872-885, (1927).

[4]Muskat and Huggins, J. Am. Chem. Soc., 51, 2496-2503, (1929).

determining the mode of addition of symmetrical and unsymmetrical addenda to these systems. It has been the purpose of the investigation reported here to study the mode of addition of hydrogen and of hydrogen bromide to the unsymmetrical conjugated compound, 1-phenyl-2,3-dimethybutadiene, 1-3.

In attempting to prepare this compound, 1-phenyl, 2,3-dimethylbutadiene-1,3 by the method recorded in the literature by Kohler,[1] McBay[2] was not successful.

The method of preparation of the compound as outlined by Kohler[3] consists of the preparation of alpha methyl cinnamic acid,[4] the conversion of this acid into its corresponding methyl ester, and the subsequent addition of two moles of methyl magnesium iodide to this ester to form the tertiary alcohol which by losing water upon distillation yields the compound, 1-phenyl-2,3-dimethylbutadiene-1,3.

Kohler[5] reports that this compound boils at 165° under 30 mm., and gives the following analysis. Subs; 0.2073; grams CO_2, 0.6917; grams H_2O, 0.1645; Calcd. for $C_{12}H_{14}$: C, 91.1, H, 8.9; Found: C,91.0, H, 9.20.

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[1]E. P. Kohler, Am. Chem. J., 36, 529 (1906).

[2]Henry C. R. McBay, "The Preparation and Bromination of 1-phenyl, 2-3 dimethylbutadiene, 1-3," (Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1936), p. 5.

[3]E. P. Kohler, op. cit., pp. 529-30.

[4]Rodger Adams, "Organic Reactions," J. Wiley & Sons, Inc., New York, 1942Col. vol. I p. 61.

[5]E. P. Kohler, op. cit., p. 529.

Recorded in the literature is the more simple method of Bogert and Davidson[1] for the preparation of the intermediate, methyl-β-methyl styryl ketone, which Kohler[2] did not isolate. Huggins and McBay[3] prepared 1-phenyl, 2-3 dimethylbutadiene by treating methyl-β-methyl styryl ketone[4] with one mole of methyl magnesium iodide in absolute ether to form the corresponding tertiary alcohol. This alcohol loses water upon distillation to yield the conjugated compound. This conjugated compound reported by Huggins and McBay[5] has the same carbon and hydrogen content and the same configuration as that reported by Kohler,[6] but was found to boil at 128° under 30 mm. Analysis[7]: Subs; 0.1400, 0.0761 ; CO_2, 0.4678, 0.2530 ; H_2O, 0.1106, 0.0599, calcd. for $C_{12}H_{14}$: C, 91.08, H, 8.85. Found: C, 91.13, 90.67: H, 8.84, 8:82.

Because of this discrepancy between the boiling points reported by these workers for this compound, 1-phenyl-2,3-dimethylbutadiene, 1-3, it was necessary to make a thorough

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[1]Bogert and Davidson, J. Am. Chem. Soc., 54, 334 (1932).

[2]E. P. Kohler, op. cit., p. 530.

[3]Henry C. R. McBay, op. cit., pp. 6-8.

[4]Ibid.

[5]Ibid., pp. 16-18.

[6]E. P. Kohler, op. cit., p. 530.

[7]Henry C. R. McBay, op. cit., p. 18.

re-examination of these methods for the synthesis of this compound before proceeding with the studies of its addition reactions. This re-examination seemed absolutely necessary in order to determine whether these compounds are the same, or if they are isomers of the same compound, or if they are different compounds so that this correction might be made in the literature. The results of this re-examination are reported in part I of this thesis.

Part II of this thesis is a report of the studies of the addition of hydrogen and of hydrogen bromide to 1-phenyl-2,3-dimethylbutadiene, 1-3.

CHAPTER II

THEORETICAL PART I

THE SYNTHESIS OF 1-PHENYL-2,3-DIMETHYLBUTADIENE-1,3, A RE-EXAMINATION

This is a report of a comparative study of the compound reported in the literature by Kohler[1] as being 1-phenyl-2,3-dimethylbutadiene-1,3, and of the compound reported by Huggins and McBay[2] with the same configuration and the same carbon and hydrogen content as Kohler's[3] compound but having a different boiling point.

The compound was prepared by the method outlined by Kohler.[4] The alpha methyl cinnamic acid used was prepared by the Perkins synthesis[5] and converted by the standard procedure to the methyl ester. This ester was in turn treated with methyl magnesium iodide. According to Kohler[6] the first mole of the Grignard reagent replaces the methoxy group in the ester with the methyl group giving the corresponding methyl ketone. This ketone, methyl-β-methyl styryl ketone,

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[1] E. P. Kohler, op. cit., p. 529.

[2] Henry C. R. McBay, op. cit., p. 18.

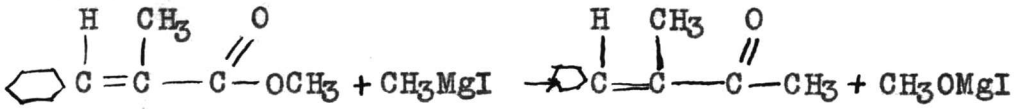
[3] E. P. Kohler, op. cit., p. 530.

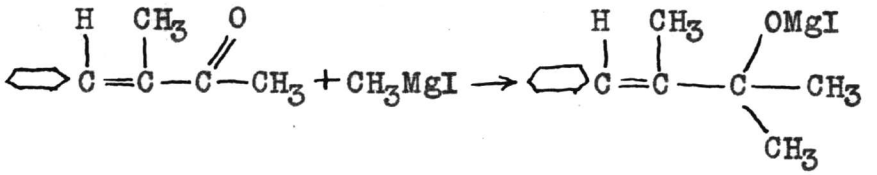
[4] Ibid.

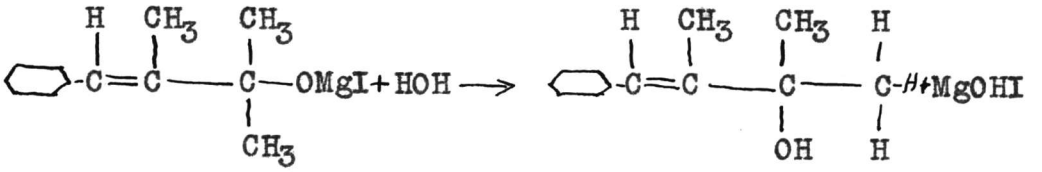
[5] Rodger Adams, "Organic Reactions," J. Wiley & Sons, Inc., New York, 1942, Col. vol. I, p. 61.

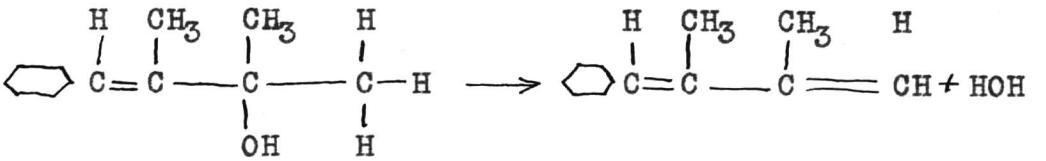
[6] E. P. Kohler, The Am. Chem. J., 36, 529 (1906).

was not isolated by Kohler. The second mole of the Grignard reagent adds to the carbonyl group in the usual manner to form the corresponding tertiary alcohol. Equations given on thes page will illustrate this method of synthesis.

1. 

2. 

3. 

4. 

Because of certain impurities, the tertiary alcohol as prepared above could not be dehydrated easily and persisted in retaining its yellow color. The hydrocarbon obtained upon dehydration of the alcohol boiled at 128° C. under 30 mm. and its refractive index was; $N_D^{20} = 1.5775$.

The 1-phenyl-2,3-dimethylbutadiene-1,3 was prepared also by the method of Huggins and McBay.[1] In this method the methyl-ℓ-methyl styryl ketone, which Kohler did not isolate,

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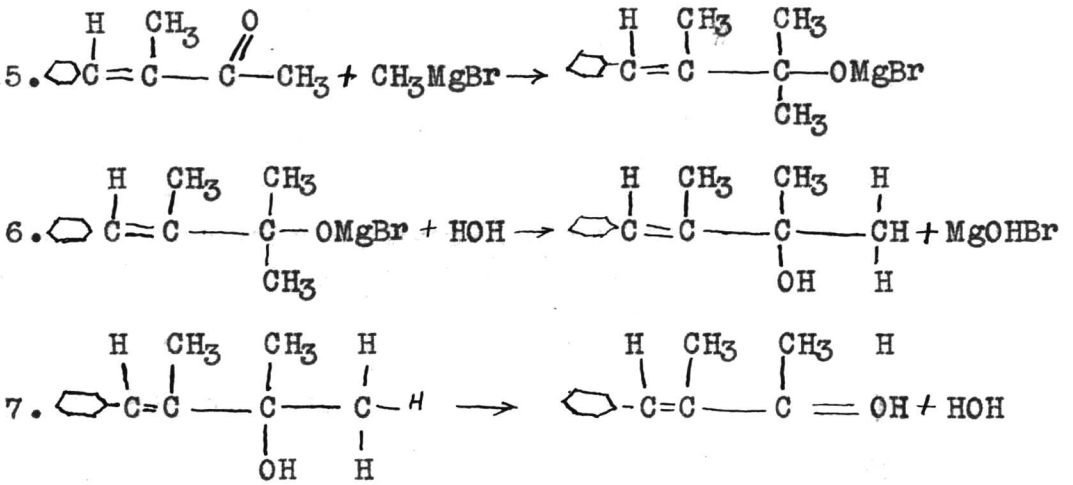
[1]Henry C. R. McBay, op. cit., pp. 6-8.

was prepared by the method of Bogert and Davidson.[1] The equations below will illustrate this method of synthesis.



The hydrocarbon made as indicated was collected at 128° C. under 30 mm. and the refractive index was; $N_D^{20} = 1.5775$.

It is important to notice here that the compound prepared by the method of Kohler does not have the constants he reports in the literature,[2] but has constants identical with those of the compound prepared by the method of Huggins and McBay.[3]

The compounds made by the methods outlined above were kept separate throughout this investigation, and were treated in the same manner in each attempt at identification and comparison under identical experimental conditions.

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[1]Bogert and Davidson, J. Am. Chem. Soc., 54, 334 (1932).

[2]E. P. Kohler, J. Am. Chem. Soc., 36, 538 (1906).

[3]Henry C. R. McBay, op. cit., pp. 7-8.

A comparative study of the vapor pressure curves of the hydrocarbon derived from the method of Huggins and McBay and of Kohler was made. In separate experiments, a series of distillations of each hydrocarbon were carried out under pressures ranging from 1-50 mm. The data obtained from these experiments are shown in Tables IA and IB below:

TABLE IA

VAPOR PRESSURE DATA FOR HYDROCARBON MADE BY METHOD OF HUGGINS AND McBAY

B. P. °C.	B. P. (abs. T)	Reciprocal $\frac{1}{T} \times 10^3$	Pressure mm.	$\log_{10}$ Pressure
74	347.00	2.882	1.5	0.17609
101	374.00	2.673	9.5	0.97772
118	391.00	2.557	20.0	1.30103
128	401.00	2.493	30.0	1.47712
134	407.00	2.457	35.0	1.54407
137	410.00	2.439	40.0	1.60206
141	414.00	2.415	50.0	1.69897

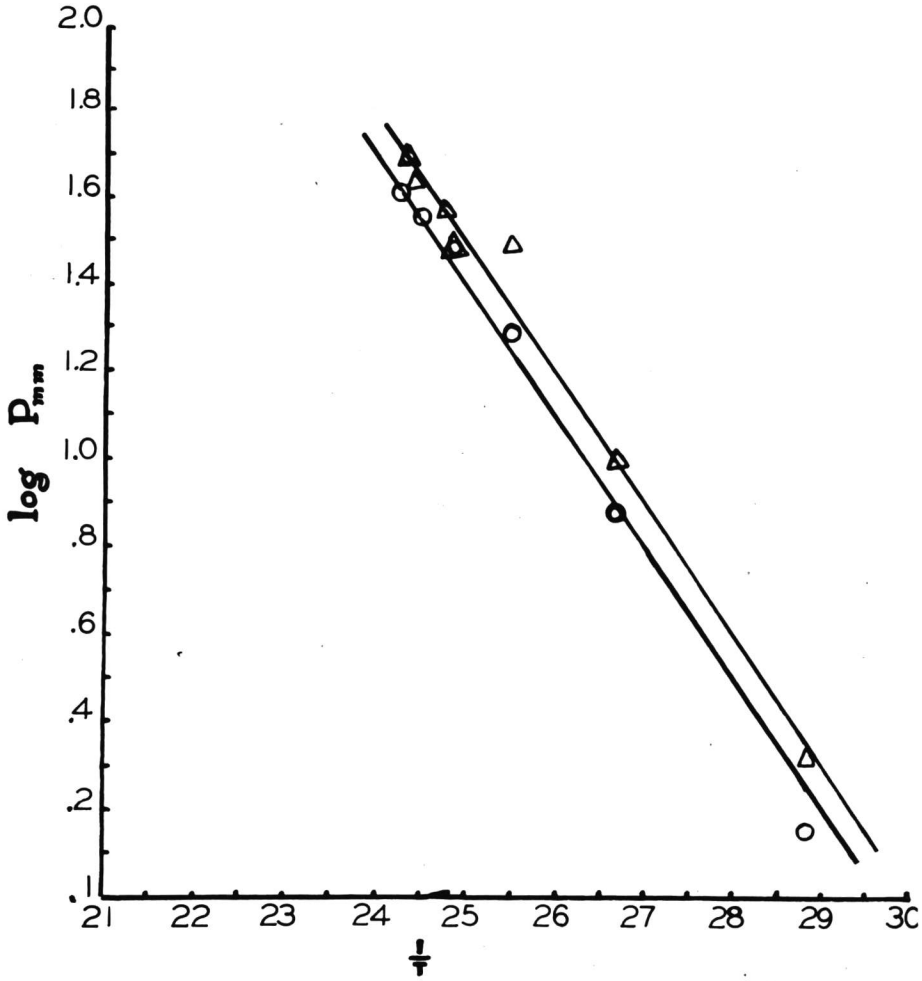
Latent Heat of Vaporization Calculated from these data = 11,950 ± 500 cal/mole.

TABLE IB

VAPOR PRESSURE DATA FOR HYDROCARBON MADE BY METHOD OF KOHLER

B. P. °C.	B. P. (abs. T)	Reciprocal $\frac{1}{T} \times 10^3$	Pressure mm.	$\log_{10}$ Pressure
74	347.00	2.882	2.0	0.30103
102	375.00	2.666	10.0	1.00000
118.5	391.50	2.554	20.0	1.30103
130.5	403.50	2.557	31.0	1.49136
133	406.00	2.463	35.0	1.54407
137	410.00	2.439	40.0	1.60206
141	414.00	2.415	50.0	1.69897

Latent Heat of Vaporization Calculated from these data = 12,102 ± 500 cal/mole



VAPOR PRESSURE CURVES FOR HYDROCARBON
Δ — PREPARED FROM ESTER (By method of Kohler)
O — PREPARED FROM KETONE

These data shown in the tables on page 8 (Table IA and Table IB) indicate that the hydrocarbon derived from each method of synthesis distills at the same temperature under equivalent pressures. From these data the Log_{10} of the vapor pressure has been plotted against the reciprocal of the absolute temperature, and the latent heats of vaporization of the hydrocarbon obtained from both methods of synthesis have been calculated. (See figure I, page 9). That the hydrocarbons obtained by these methods of synthesis have been essentially pure is indicated by the constancy of the slopes of the vapor pressure curves (Figure I). The fact that the slopes of the two curves are the same indicates the identity of the heats of vaporization of the two hydrocarbons.

The "Diels and Alder"[1] derivative has been widely used as a test for conjugation in simple organic compounds.* This method consists of the addition of the 1-4 positions of the conjugated compound to the double bond in any one of a number of suitable reagents called dieneophiles. Many of these reagents are listed by Allen.[2] Maleic anhydride was successfully used as the dieneophile in this investigation.

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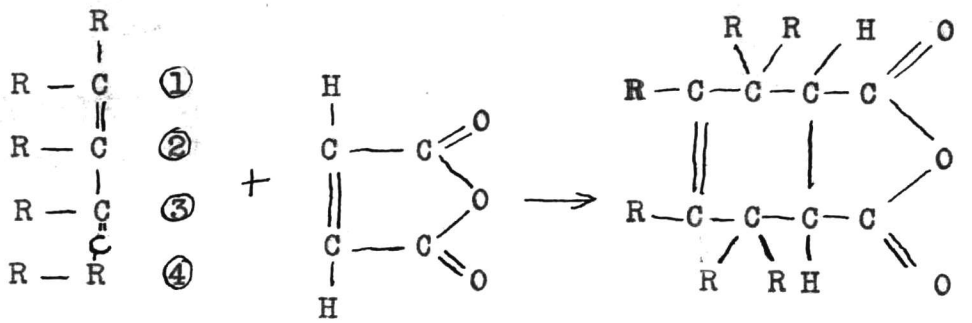
[1]Charles F. Allen, J. Chem. Educ., 10, 494-97 (1933).

[2]Ibid.

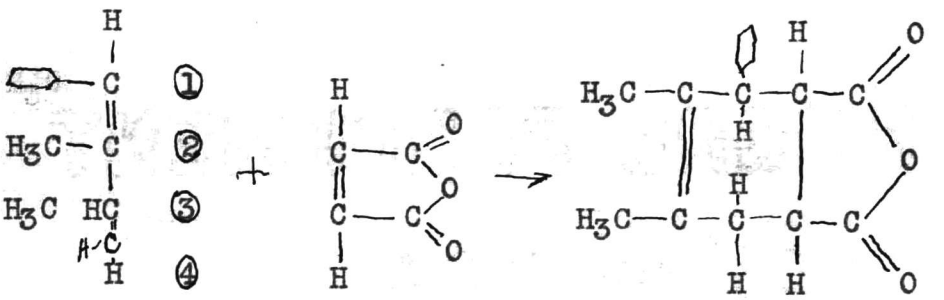
*There have been reported significant exceptions to this general rule. For examples where maleic anhydride has been added to certain non-conjugated compounds see; Ross, Gebhart, and Gerecht, J. Am. Chem. Soc., 68, 1373 (1946) Bergmann, Szmuszkowicz, and Fauncz, J. Am. Chem. Soc., 69, 1773 (1947).

The addition results in the tying-in of the ends of the conjugated molecule to form a ring with the subsequent shifting of the double bond to the center of molecule. This mechanism may be illustrated by this equation.

8. 

These resulting compounds make suitable derivatives because they are recrystallizable solids with sharp melting points.

The maleic anhydride derivatives of the hydrocarbons from both sources were prepared and found to have identical melting points (127-128°C.) The melting point of a mixture of these two derivatives was also 127-128°C. Huggins and McBay[1] reported the melting point of this derivative to be 131-132°C. The equation representing the formation of this derivative follows:

9. 

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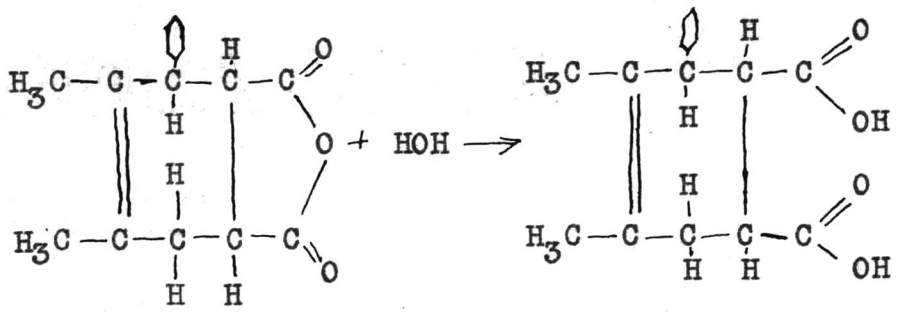
[1]Henry C. R. McBay, op. cit., pp. 9-10.

In order to prove that this "Diels and Alder" derivative whose melting point was close to that of maleic anhydride was not maleic anhydride, both derivatives were hydrolyzed according to the following equation to the corresponding dicarboxylic acids by recrystallizing them from water.

10. 

These acids resulting from the hydrolyses, as well as a mixture of these acids, were found to melt at 207°C. Huggins and McBay[1] reported the melting point of this acid to be 209°C. Table II summarizes these results.

It is significant to note here that while Huggins and McBay heated the reagents maleic anhydride and 1-phenyl-2,3-dimethylbutadiene,1-3 together in thiophene free benzene for 24 hours under reflux conditions to obtain the "Diels and Alder" derivative, they observed a color change from colorless to pale yellow immediately upon mixing these reagents. This suggested to the investigator that these compounds might have reacted immediately upon mixing, or at least that such prolonged heating might be unnecessary. Accordingly, the maleic

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[1]Henry C. R. McBay, op. cit., p. 19.

TABLE II

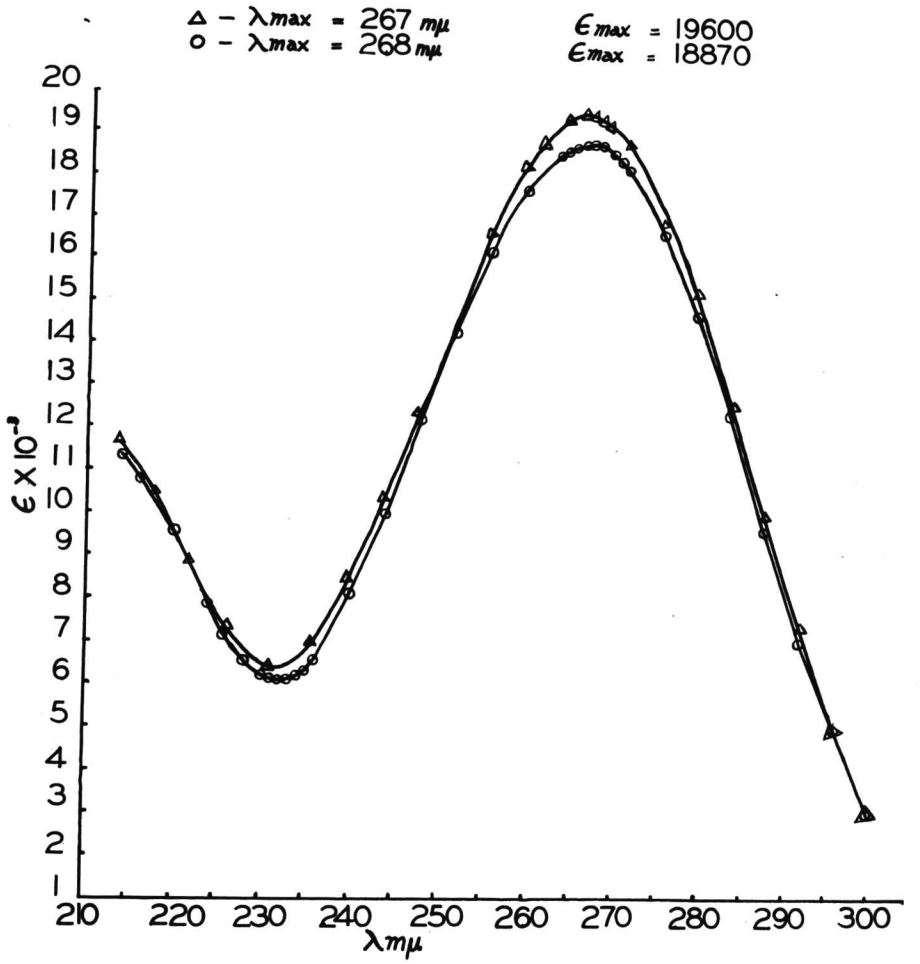
MELTING POINTS OF "DIELS AND ALDER" ANHYDRIDE AND DICARBOXYLIC ACID DERIVATIVES

Results Obtained By	Product Melted	M. P. of Anhydride	M. P. of Dicarboxylic Acid
Moore	Maleic anhydride derivative of hydrocarbon obtained by method of Kohler	127-128°C	206-207°C
	Maleic anhydride derivative of hydrocarbon obtained by method of Huggins and McBay	127-128°C	207°C
Huggins and McBay	"	131-132°C	209°C

anhydride derivatives reported here were successfully prepared without the application of heat simply by allowing these reagents to stand in the solvent at room temperature for seven days.

Molecular weight determinations of the hydrocarbons derived from both methods of synthesis were carried out using the freezing point technique with benzene as a solvent. Within experimental error, the results obtained checked with the calculated value for the formula $C_{12}H_{14}$. These data are shown in the table of physical constants (Table IIIA).

The values for the refractive indices of the hydrocarbons from each source were determined. The values checked with



Absorption Curves of Hydrocarbon

Δ – PREPARED FROM ESTER (By method of E. P. Kohler)

o – PREPARED FROM KETONE

FIGURE II

each other. (See Table IIIA, Physical Constants).

TABLE IIIA

PHYSICAL CONSTANTS OF HYDROCARBON
1-PHENYL-2,3-DIMETHYL BUTADIENE-1,3.

Constant	M. W. Calcd.	M. W. Obsv'd.	B. P.	20^{o} Density	Refractive Index, N_D^{20}
Hydrocarbon made by Method of E. P. Kohler	158	154.2	128^{o}C/ 30 mm.	0.926	1.5775
Hydrocarbon made by Method of Huggins and McBay	158	153.8	128^{o}C/ 30 mm.	0.928	1.5775

TABLE IIIB

PHYSICAL CONSTANTS OF ALCOHOL
1-PHENYL-2,3-DIMETHYL-3-HYDROXY BUTENE-1

Constant	Boiling Point	Refractive Index N_D^{20}
Alcohol made by method of Kohler	$102\text{-}103^{o}$C./ 2mm.	1.5620*
Alcohol made by method of Huggins and McBay	$103\text{-}104^{o}$C./ 2mm.	1.5670*

*The discrepancy in these refractive indices is due to the difficulty in preventing dehydration of the alcohol upon distillation.

The absorption spectra of these hydrocarbons prepared by both methods of synthesis have been studied for comparison.

These data shown in Figure II (Page 14) show that within experimental error the absorption curves of the two hydrocarbons are identical.

These hydrocarbons, one prepared by the method of Kohler[1] and one prepared by the method of Huggins and McBay,[2] have identical boiling points, heats of vaporization, densities, molecular weights, refractive indices, "Diels and Alder" (maleic anhydride) derivatives, and absorption spectra. These facts force one to the conclusion that the compounds are identical. The constants reported in the literature by E. P. Kohler[3] for the compound, 1-phenyl, 2-3 dimethylbutadiene, 1-3 are therefore in error due either to experimentation or to a misprint.

Some recent work on the mechanisms of Grignard reactions by Kharasch, Morrison, and Urry[4] suggests that the erroneously high boiling point reported by Kohler for the hydrocarbon, 1-phenyl-2,3-dimethylbutadiene, 1-3 might be due to polymerization of the conjugated compound enhanced by the presence

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[1]E. P. Kohler, op. cit., pp. 529-31.

[2]Henry C. R. McBay, op. cit., pp. 6-8.

[3]E. P. Kohler, op. cit., p. 529.

[4]Kharasch, Morrison, and Urry, J. Am. Chem. Soc., 66, 368 (1944)
See also,
Kharasch and Urry, J. Org. Chem., 13, 101-4 (1948).

of the free radicals from the possible source---

11. $CH_3 : MgI \longrightarrow CH_3^{\cdot} + {\cdot}MgI$

This homolytic dissociation of the Grignard reagent might well have taken place in Kohler's work, since the literature reveals that at the time of his work it was the usual procedure to carry out Grignard reactions under conditions of vigorous reflux. Since the work of Kharasch, Morrison, and Urry[1] is reported long after Kohler's work was done, Kohler could hardly have been aware of this possible difficulty. Kharasch, Morrison, and Urry[2] have demonstrated that CH_3MgBr does not undergo such homolytic dissociation to produce free radicals as readily as does methyl magnesium iodide. Hence a study was made, the purpose of which was to compare the yields of alcohol and of polymerized material resulting from the treatment, under identical conditions, of the ester with CH_3MgI (Kohler's method) and with CH_3MgBr. It is important to state here that a special attempt was made here to minimize the probability of encountering the difficulty suggested above by conducting these experiments under conditions of minimum instead of maximum reflux.

The same study was made using instead of the ester the

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[1] Ibid.

[2] Kharasch, Morrison and Urry, op. cit., pp. 101-4 (1948)

ketone. (Method of Huggins and McBay). The results of these comparative studies are given in tabulated form below.

TABLE IV

GRIGNARD EXPERIMENTS

Compound	Moles	Grignard Reagent	Hydrolytic Reagent	Per cent Yield Alcohol	Polymerization
Ketone	.55	CH_3MgBr	25%NH_4Cl	89.76	2.5g.
Ester (Kohler)	.54	"	"	59.61	10.1g.
Ketone	.33	CH_3MgI	"	68.51	11.1g.
Ester	.31	"	"	48.60	17.1g.
Ketone	.55	CH_3MgBr	25%H_2SO_4	78.64	8g.
Ester	.54	"	"	47.68	18.6g.
Ketone	.27	CH_3MgI	"	47.67	18.9g.
Ester	.26	CH_3MgI	"	34.51	26.1g.

These data show that the percentage yield of the tertiary alcohol was greater in each experiment where the ketone was used, using either CH_3MgBr or CH_3MgI as the Grignard reagent. It is interesting to notice here that when 25% H_2SO_4 was used as a hydrolytic reagent, the yield of the alcohol from both the ketone and the ester was reduced, but to a greater extent when the ester was used. In each experiment where CH_3MgBr was used as the Grignard reagent greater yields of the alcohol were obtained from both the ester and the ketone. It is also important to observe that regardless of the type of Grignard reagent used the yield of alcohol from the ketone was greater than that from the ester.

Where 25% NH_4Cl was used for hydrolysis of the Grignard complex and CH_3MgBr was used as a Grignard reagent, very little polymerization was observed from either the ketone or the ester. In experiments, however, where CH_3MgI was used and the Grignard complex hydrolyzed over 25% NH_4Cl solution, some polymerization was observed from the ester but less from the ketone. Polymerization was very prominent in each experiment where 25% H_2SO_4 was used as a hydrolytic reagent using ether CH_3MgI or CH_3MgBr as a Grignard reagent. Important also is the fact that polymerization was very prominent when CH_3MgI was used, but to a greater extent when the tertiary alcohol was made from the ester.

Mention should be made here of the several techniques employed in attempts to dehydrate the tertiary alcohol. The alcohol was repeatedly distilled under reduced pressure, and in keeping with the results obtained by Huggins and McBay[1] this alcohol during distillation lost water which was observed in the condenser. The number of distillations required to dehydrate completely the alcohol may be reduced by using fused potassium aluminum sulfate as a catalyst. The completely dehydrated hydrocarbon was collected at 128°C. under 30 mm. This compound was a clear colorless oil. In some instances dehydration of the alcohol was accomplished by refluxing the alcohol in benzene solution for several hours over fused potassium aluminum sulfate.

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[1]Henry C. R. McBay, op. cit., p. 6.

This dehydration has also been accomplished by allowing the alcohol to stand in contact with benzoyl chloride, propionyl chloride, or acetyl chloride. This last method using acid chlorides seems to be most effective.

CHAPTER III

THEORETICAL PART II

THE ADDITION OF HYDROGEN AND OF HYDROGEN BROMIDE TO 1-PHENYL-2,3-DIMETHYLBUTADIENE-1,3

Workers[1] have studied extensively the addition reactions of chlorine, bromine, hydrogen and the halogen acids to 2,3 dimethylbutadiene-1,3 and report that these addenda add to this compound predominantly at the one and four positions, (1-4 addition).

12. $HC(H)=C(CH_3)-C(CH_3)=CH(H) + AB \longrightarrow HC(H)-C(CH_3)=C(CH_3)-CH(H)$

(AB = X_2 or AB = HX)

A B

It has been reported that phenylbutadiene adds bromine[2] and chlorine[3] at the three and four positions, (3-4 addition). Huggins and McBay[4] report that the unsymmetrical compound 1-phenyl, 2-3 dimethylbutadiene, 1-3 (I) adds bromine at the three and four positions, (3-4 addition). Huggins and Gandy[5]

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[1]For a review of this work see C. H. F. Allen, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1943, H. Gilman editor, p. 669.

[2]Strauss, Ber., 42, 2866 (1909).

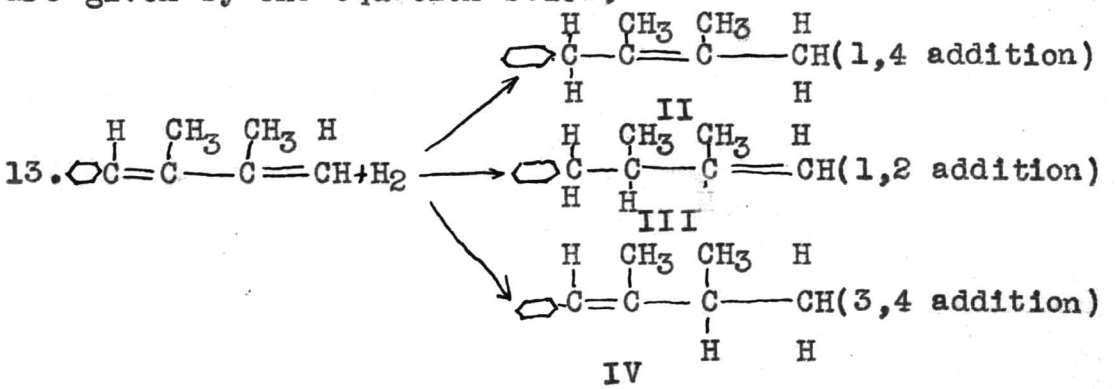
[3]Muskat and Huggins, J. Am. Chem. Soc., 51, 2496 (1929).

[4]Henry C. R. McBay, "The Preparation and Bromination of 1-Phenyl-2,3-Dimethylbutadiene-1,3" (Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1936), p. 23.

[5]David Conrad Gandy, "The Course of Reduction of 1-Phenyl Butadiene and 1-Phenyl-3-Methyl Butadiene-1,3" (Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1942), pp. 1-23.

have studied the course of reduction of 1-phenyl-butadiene and of 1-phenyl-3-methylbutadiene-1,3. It appeared then, that it would be interesting to investigate the modes of orientation of hydrogen and of hydrogen bromide into the conjugated compound 1-phenyl-2,3-dimethylbutadiene-1,3. A report of this investigation is given in the following pages.

The several possible modes of orientation of hydrogen are given by the equation below:



One must bear in mind the fact, however, that it is possible for any two or all three of these reactions to proceed simultaneously, giving a mixture of these olefines.

If these compounds are treated with ozonized oxygen or oxidized with potassium permanganate, they should be broken down into fragments the identification of which would point to the type of addition that had taken place.

The 1-phenyl-2,3-dimethylbutadiene-1,3 (prepared by the methods described in Part I of this thesis) was treated with one mole of hydrogen, using absolute methyl alcohol as a solvent and Raney nickel[1] as a catalyst. The apparatus

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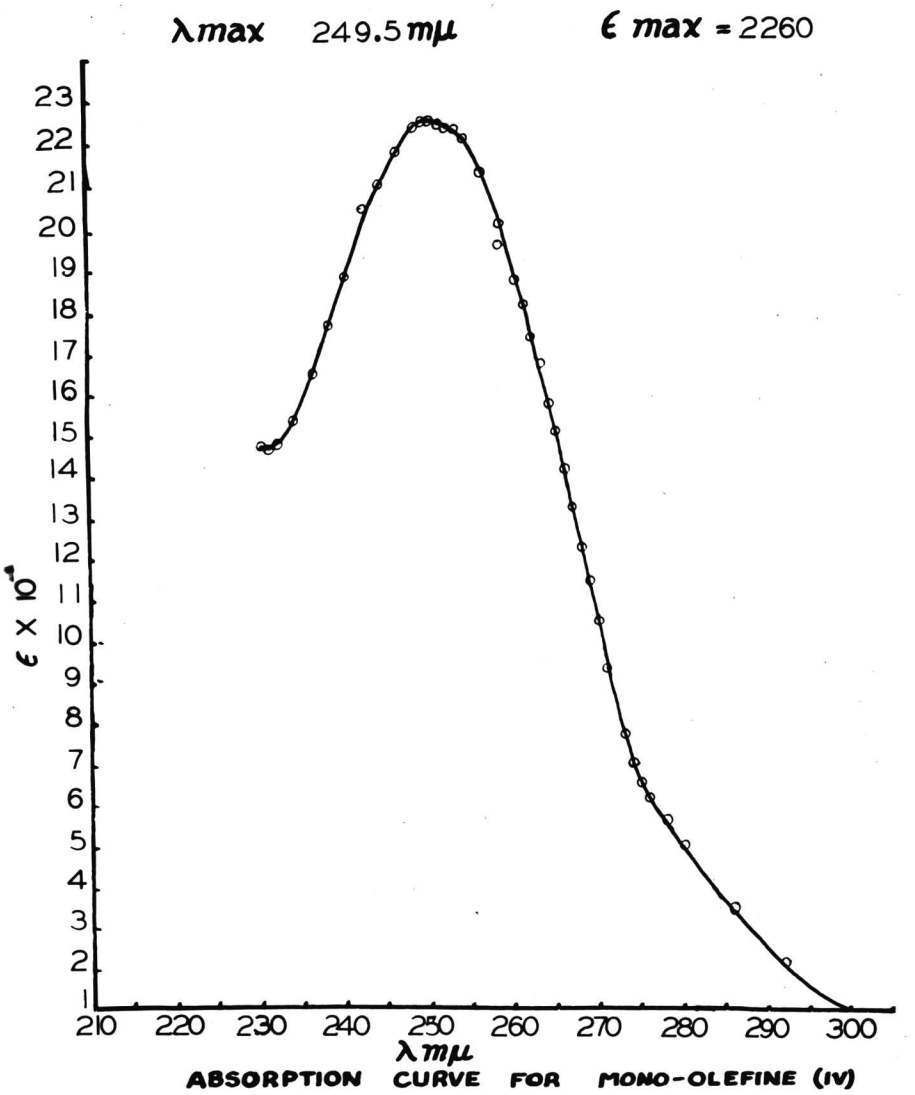
[1]Cavert and Adkins, J. Am. Chem. Soc., 54, 4116 (1932).


λmax 249.5 mμ
ε max = 2260
ε X 10⁻³
23
22
21
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12
11
10
9
8
7
6
5
4
3
2
1
210
220
230
240
250
260
270
280
290
300
λ mμ
ABSORPTION CURVE FOR MONO-OLEFINE (IV)

FIGURE III

described by Adams and Voorhees[1] was used for this experiment. A clear colorless oil, the mono-olefine, was obtained by this reduction. This compound boils at 54°C. under 2 mm.

Some special comment on the purification of this mono-olefine is necessary. Although at a pressure of 1.5 mm. 1-phenyl-2,3-dimethylbutadiene-1,3 boils approximately 16°C higher than the mono-olefine (hydrogen adduct of the hydrocarbon), the technique of distillation was not an advisable method for removing the last traces of the diene left after its partial reduction. Since isolated double bonds frequently migrate into conjugation when their compounds are heated, a method of purification of the mono-olefine was desirable whose application and efficiency require a minimum of heating. In this case the Diels-Alder[2] condensation reaction satisfies this requirement. (See Part I of this thesis). Thus the last traces of the hydrocarbon were removed from the reduction product by prolonged shaking with maleic anhydride at room temperature. The absorption spectra of this mono-olefine has been measured, and the curve representing this data is shown in Figure III on page 23.

The fragments expected from the oxidation of each of the three possible products (mono-olefines) obtainable from the addition of hydrogen to 1-phenyl-2,3-dimethylbutadiene-1,3 (I) are indicated by the following equations.

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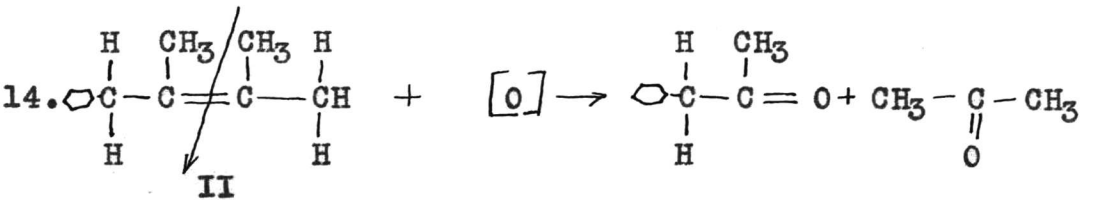
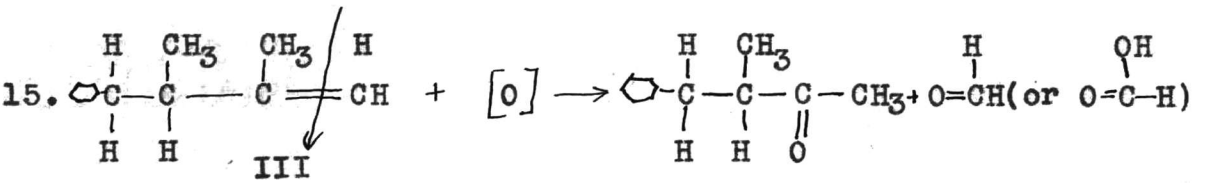
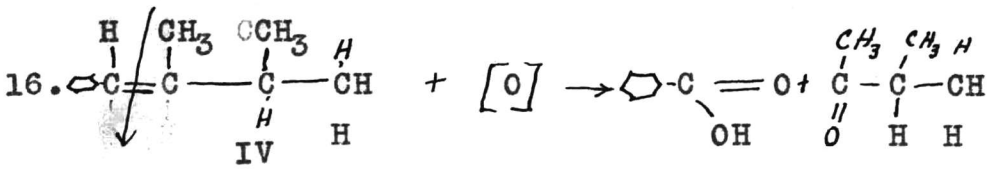
[1] Gilman and Blatt, "Organic Synthesis," John Wiley & Sons, Inc., New York, 1941, Col. vol. I p. 61.

[2] Allen, J. Chem. Educ., 10, 494 (1933).

14. 

15. 

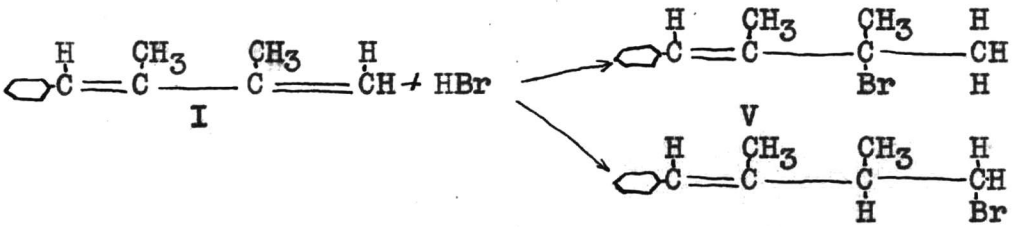
16. 

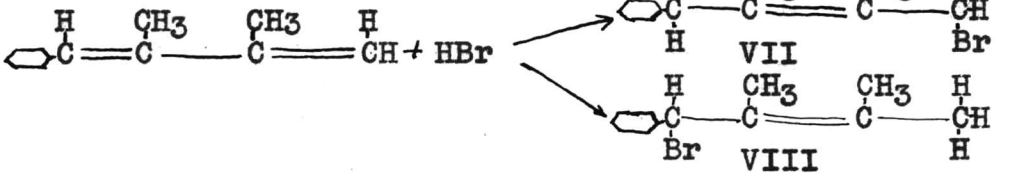
If one is able to isolate and identify either 1-phenyl-propanone-2 or acetone, it is evidence that 1-4 addition has occurred. This can be seen from equation 14. The isolation and identification of formaldehyde or 3-methyl-4-phenylbutanone-2 would give evidence that 1-2 addition had taken place. Equation 15 indicates the formation of these products. If benzaldehyde, benzoic acid, or iso-propyl methyl ketone are isolated and identified, this would indicate the fact that some 3-4 addition occurred, according to equation 16.

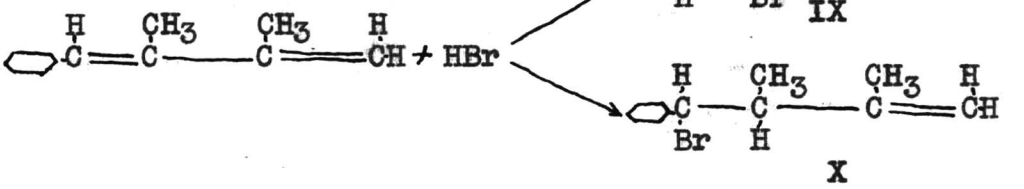
In good yields benzoic acid has been isolated from the fragments and identified as one of the oxidation products of this dihydro-derivative obtained by reduction of 1-phenyl-2,3-dimethylbutene-1,3. It is therefore suggested that the structure of this dihydro addition product is 1-phenyl-2,3-dimethylbutene-1 (IV), and that the addition of hydrogen to 1-phenyl-2,3-dimethylbutadiene-1,3, in the presence of Rancy nickel has taken place at the carbon atoms number three and four, (3-4 addition).

It should be stated here that in no case was the investigator able to isolate and identify any methly iso-propyl ketone as would be expected. It might have been that the methyl iso-propyl ketone was destroyed by the techniques used in oxidation of the mono-olefine, or that the ketone undergoes some type of rearrangement. No attempts were made, however, in this investigation to study this difficulty.

The possible modes of addition of hydrogen bromide to 1-phenyl-2,3-dimethylbutadiene-1,3, are given in the equations below:

17. 

18. 

19. 

The preparation of pure dry hydrogen bromide was accomplished by the use of a modification of the method reported by D. R. Duncan,[1] in Inorganic Synthesis. Using several

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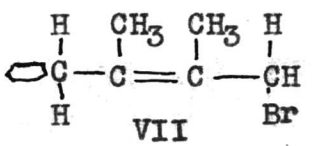
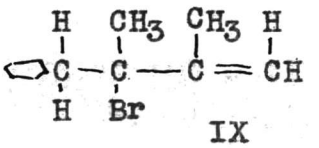
[1] H. S. Booth, "Inorganic Synthesis," McGraw Hill Book Co., New York, (1939), Vol. I p. 151.

different solvents and working under anhydrous conditions, hydrogen bromide prepared in this manner was added to 1-phenyl-2,3-dimethylbutadiene-1,3. The hydrobromide adduct thus obtained is an extremely unstable oil. When subjected to distillation at reduced pressure it lost hydrogen bromide at pressures as low as 0.5 mm.

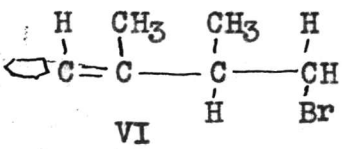
The problem of determining the mode of orientation here displayed by hydrogen bromide is exceedingly complicated. The hydro-bromide has not been obtained in the pure state entirely free from unsaturated hydrocarbons. It has occurred to the investigator that the position of the bromine might be tagged by applying to the mixture the Grignard technique followed by carbonation with CO_2. However, the results from such an attempt to tag the position of the bromine atom in this impure adduct would for the following two reasons (a and b) be meaningless. (a) Of the six possible structures this hydro-bromide adduct might have, four of these contain an allylic bromine, (bromine attached to carbon adjacent to a doubly bonded carbon).



VII



IX



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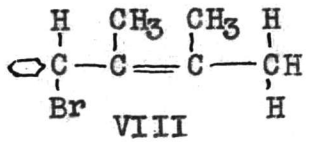

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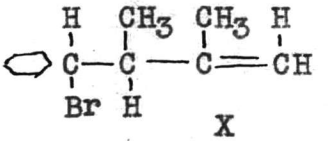
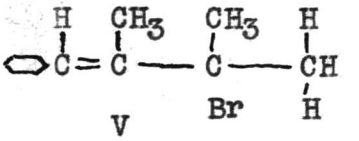


X



V

Any attempt to replace this bromine atom in such molecules by the use of the Grignard reaction or any other polar mechanism

will give rise to conditions necessary for the well-known allylic rearrangements. (b) Because of the presence of unsaturated hydrocarbon impurities difficult to remove, the technique of oxidative degradation would here also lead to unreliable conclusions. In the face of these difficulties, the further elucidation of this problem has been temporarily abandoned. At the time of this writing it can only be said that dry hydrogen bromide in benzene reacts with 1-phenyl-2,3-dimethylbutadiene-1,3 to form an extremely unstable compound.

CHAPTER IV

EXPERIMENTAL

Preparation of Solvents.

Anhydrous Ether - The ether was distilled off of concentrated sulfuric acid,[1] dried over calcium chloride and finally over metallic sodium.

Thiophene-Free Benzene - Large volumes of benzene were washed with small volumes of concentrated sulfuric acid until no color appeared in the acid layer. The benzene was then washed several times with 15% sodium carbonate, and finally with distilled water. It was then dried over calcium chloride for several days and finally distilled off of sodium through a 32 cm. column packed with single turn glass helixees.

Methyl Alcohol and Ethyl Alcohol - The absolute alcohols used were prepared in the usual manner, being refluxed for at least 24 hours over calcium oxide and distilled through a 20 cm. fractionating column.

Pyridine - The pyridine was distilled off of potassium hydroxide at atmospheric pressure. The fraction boiling between 115-116°C. was used.

Carbon Tetra-Chloride - This compound was washed successively with 20% potassium hydroxide (to remove the sulfur),

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[1] L. I. Feiser, "Experiments in Organic Chemistry," 2d ed., D. C. Heath and Co., New York, 1941, p. 361.

concentrated sulfuric acid, 10% sodium carbonate and distilled water. It was dried over calcium chloride and finally distilled off of anhydrous calcium sulfate, (Hammond's Drierite).

The Preparation of ∝ Methyl Cinnamic Acid and the Corresponding Methyl and Ethyl Esters. The ∝ methyl cinnamic acid used was prepared by the Perkin Synthesis[1] and was converted by standard procedures into the corresponding ester. The ethyl ester of ∝ methyl cinnamic acid prepared in this manner was a colorless oil which boiled at 115°C./ 5 mm., N_D^{20} = 1.5475). The methyl ester of ∝ methyl cinnamic acid prepared in this manner was distilled and collected between 108-109°C./ 3 mm. This ester solidified at room temperature into a white crystalline solid which melted at 34.8°C., (Literature M. P., 34.9°C.).

The Preparation of Methyl-β-Methyl Styryl Ketone. The methyl-β-methyl styryl ketone used was prepared by the method of Bogert and Davidson.[2]

The Preparation of 1-Phenyl-2,3-Dimethyl-3-Hydroxy Butene-1. (Method of Huggins and McBay). The methyl-β-methyl styryl ketone prepared by the method indicated above was treated with 20% more than the theoretical amount of methyl magnesium iodide or methyl magnesium bromide required for equimolar quantities. The methyl magnesium bromide was

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[1] Radger Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, 1942. Col. Vol. I p. 241.

[2] Bogert and Davidson, J. Am. Chem. Soc., 54, 334 (1932).

prepared in the usual manner, using a Grignard flask fitted with an upright condenser, dropping funnel, mercury seal, and mechanical stirrer. The ketone, methyl-β-methyl styryl ketone, in ethereal solution was added drop-wise to the Grignard reagent, and the resulting product was allowed to stand overnight. This product was hydrolyzed over a 25% solution of ammonium chloride. In some experiments 25% cold sulfuric acid solution was used as the hydrolytic agent. During hydrolysis the system was kept in a salt ice bath with constant shaking. The resulting layers were separated in the separatory funnel, and the water layer was extracted several times with ether. These extracts were added to the main etheral solution, and the combined extracts were washed (in cases where sulfuric acid was used, with sodium carbonate) with distilled water and dried over calcium chloride for approximately seven hours.* The solution was then filtered into a dry distilling flask, and the ether was removed by suction from the water pump or by heating over a water bath. The resulting alcohol, 1-phenyl-2,3-dimethyl-3-hydroxybutene-1, remained in the flask. This alcohol was distilled under reduced pressure and finally collected at 104-105°C./ 2mm; 117-119°C./ 7mm. It was a bright yellow oil, $N_D^{20} = 1.5670$.

(Method of Kohler). Both the methyl ester and the ethyl esters of α methyl cinnamic acid prepared as described above were treated in separate experiments with the theoretical

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*If the etheral solution is allowed to stand over calcim chloride for too long a period of time, upon distillation of the alcohol polymerization is more prominent.

amount of methyl magnesium bromide or methyl magnesium iodide in the same manner as was the methyl-β-methyl styryl ketone described immediately above, and the alcohol, 1-phenyl-2,3-dimethyl-3-hydroxybutene-1, was obtained in 60% yields, with identical boiling points and color as the alcohol obtained from the methyl-β-methyl styryl ketone. The yields, however, were greater in each preparation where methyl magnesium bromide was used. In some experiments where methyl magnesium iodied was used the etheral solution of the alcohol was deeply colored. This color was removed by washing the ethereal solution with 10% aqueous sodium thio-sulfate.

The Preparation of 1-Phenyl-2,3-Dimethyl Butadiene-1,3. The yellow alcohol described above was converted into the hydrocarbon by the removal of a mole of water by several methods.

Method One. The alcohol was less stable when sulfuric acid was used for hydrolysis, for in this case there was evidence of the loss of water when the last traces of ether were being removed over the water bath. The complete loss of the mole of water was accomplished simply by distilling the alcohol several times under reduced pressure. The hydrocarbon resulting from this distillation was a clear colorless oil which boils at 128°C./ 30mm.

Method Two. The mole of water was removed from 1-phenyl-2,3-dimethyl 3-hydroxy butene-1 readily when the alcohol was distilled three or more times under reduced pressure using potassium aluminum sulfate as a catalyst according to the

method of Kyriakides.[1]

Method Three. Small volumes of the alcohol were dissolved in thio-phene free benzene as a solvent and refluxed gently for four hours over potassium aluminium sulfate. Water was observed in the reflux condenser during this procedure. The benzene was removed at reduced pressure using the water pump while heating the system with a water bath. The residue was placed in a round-bottom flask and distilled through a 20 cm. Vigreaux column. The hydrocarbon, a colorless oil, was collected at 128°C/ 30mm, N_D^{20} = 1.5775.

Method Four. Acetyl, benzoyl and propionyl chloride were used successfully in dehydration of the alcohol. The alcohol (1-phenyl-2,3-dimethyl-3-hydroxybutene-1), (50 grams), was placed in a 250 cc. Erlenmeyer flask and to this was added 30-35 cc. of the acid chloride. The flask became warm immediately and after several minutes drops of water could be seen in the bottom of the flask and in the condenser. This mixture was allowed to stand at room temperature for two days; and, when benzoyl chloride was used, at the end of this period a white precipitate was observed in the bottom of the flask. This precipitate was filtered off with suction from the water pump, and was identified as benzoic acid. (M. P. 121°C). The filtrate, containing the mixture of hydrocarbon and the unchanged acid chloride, was placed in a heavy glass bottle and 30 cc. of a 10% solution of sodium hydroxide was added.

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[1]Kyriakides, J. Am. Chem. Soc., 36, 980 (1914)

This mixture was shaken for 40 hours on the shaking machine. This mixture was taken up in ether, washed with a 10% solution of sodium carbonate, with distilled water, and dried over calcium chloride for several hours. The ether was removed by means of distillation with suction from the water pump while being heated on a water bath. The diene (37.2 g.) resulting from this dehydration was finally distilled and collected at 74°C/ 2mm. It was a clear colorless oil, N_D^{20} = 1.5775.

Determination of the Physical Constants of 1-Phenyl-2, 3-dimethylbutadiene-1,3. Molecular weight determinations were made by the freezing-point method using thiophene-free benzene as the solvent.

The Absorption Measurements* were made on a model DU Beckman Ultraviolet Spectrophotometer. Absolute ethyl alcohol has been used as the solvent. The concentrations of the solutions used have been of the order of 10^{-3} - 10^{-6} moles / liter.

Activation of Raney Nickel Catalyst. The activation of the Raney nickel catalyst was accomplished according to the method of Cavert and Adkins.[1]

The distillations for heat of vaporization studies were made through a 32 cm. Vigreux column.

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*These measurements were made by Dr. Lloyd N. Ferguson of the Department of Chemistry, Howard University, Washington, D. C.

[1]Cavert and Adkins, J. Am. Chem. Soc., 54, 4116 (1932)

The Preparation of the Diels and Alder Derivative, 2-Phenyl-3,4-Dimethyl-1,2,5,6-Tetra hydro-ortho-phthalic anhydride. Two grams (2g.) of the hydrocarbon, 1-phenyl-2,3-dimethylbutadiene-1,3, were dissolved in 30 cc. of dry thiophene-free benzene in a dry 100 cc. Erlenmeyer flask. A solution of maleic anhydride (1.2g.) dissolved in benzene (just enough to dissolve the anhydride) was filtered into the flask containing the benzene solution of the hydrocarbon. Immediately a yellow color appeared in the flask. The flask was stoppered and allowed to stand at room temperature for seven days. The benzene was removed by vaporization under reduced pressure. The white solid which remained was recrystallized from carbon tetra-chloride and finally from dioxane. In each case of recrystallization no heat was applied. The white compound was dissolved in sufficient amounts of solvent, and then the solvent was allowed to evaporate at room temperature or was removed by vaporization under reduced pressure. The white crystals were dried in a vacuum desicator over sulfuric acid and were found to melt at 127-128°C.

The results of these experiments were identical where the diene obtained from ether or both sources was used,* M. P. 128°C. The solid cyclic anhydride, 2-phenyl-3,4-dimethyl-1, 2,5,6-tetra hydra ortha phthalic anhydride, (1.5g.) was dissolved in 75 cc. of distilled water by heating for several hours. After all of the substance had dissolved the mixture was filtered while hot and allowed to cool. The white crystals

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*See Table II page 12.

which settled out upon cooling were filtered, placed in an Abderhalden drying pistol and dried for several hours under vacuum. The melting point of this dicarboxylic acid was 207°C.

The Preparation of 1-Phenyl-2,3-Dimethyl Butene-1. Approximately 1 gram of activated Raney nickel was poured into a thick glass bottle containing a mixture of 27.1 g. of the hydrocarbon (1-phenyl-2,3-dimethyl butadiene-1,3) dissolved in 200 cc. of absolute methyl alcohol. The apparatus used is described by Adams and Voorhees.[1] To this was added hydrogen under 45 lbs. of pressure at room temperature until the calculated pressure drop (15 lbs.) was registered on the pressure guage. The time consumed for this addition reaction was approximately fifteen minutes. After the first five minutes of this time the reaction bottle was very warm. This temperature persisted throughout the course of the reaction. The alcoholic solution was decanted off and placed in a 250 cc. round-bottom flask. The solvent was removed by means of distillation at reduced pressure from the water pump while heating on a water bath. The remaining liquid was distilled through a 20 cm. Vigreux column under reduced pressure and finally collected at 54°C. under 1.5 mm. This compound (1-phenyl-2,3-dimethylbutene-1) a mono-olefine, was

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[1]Golman & Blatt, "Organic Synthesis," Col. Vol. I, Sec. Ed. John Wiley and Sons, New York, 1941, Col. Vol. I p. 61.

a clear colorless oil.

The refractive index was N_D^{30} = 1.5062.Anal: Subs., 0.0289, 0.0407:CO_2, 0.0951, 0.1341:HOH, 0.0281, 0.0373 calcd. for $C_{12}H_{16}$: C, 89.94, H, 10.05 Found: C, 89.85,89.84:H, 10.88, 10.36

Bromination of 1-Phenyl-2,3-Dimethyl Butene-1. Several attempts were made to add the calculated amount of bromine to samples of the mono-olefine dissolved in carbon tetra chloride as the solvent. The mono-olefine (8.6510 grams) was dissolved in 75 cc. of carbon tetrachloride, and the mixture was placed in a 250 cc. dry filtering flask fitted with a drying tube attached to the side arm. Through a rubber stopper in the top of the flask was inserted the stem of a burette containing the carbon tetrachloride solution of bromine.* The titration was carried out in an ice bath, and the bromine solution was added dropwise with constant shaking. When the calculated amount of bromine solution (83.53 cc.) had been added, a color change was noted indicating that the point of saturation had been reached. This solution was allowed to stand for a few minutes in the ice bath when it was observed that the color (brown) was disappearing from the solution. This color completely disappeared and would reappear upon addition of more of the bromine solution. This was continued until 123.99 cc. of the bromine solution had been added. During the process of the addition of the excess

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*This solution was prepared by titrating from a burette 5.01 cc. of bromine (15.531 g.) into carbon tetrachloride and diluting with carbon tetrachloride to a total volume of 150 cc.

bromine solution hydrogen bromide was observed to escape through the drying tube attached to the side arm of the reaction vessel. This was probably due to the fact that the mono-olefine contained a tertiary hydrogen atom adjacent to a bromine atom in the molecule. The solvent was removed by means of distillation at reduced pressure using a water pump while heating by means of a water bath. The mixture was distilled under reduced pressure. A large soda lime tower (35 cm. high) was used in the system between the receiving flask and the vacuum pump. There was an evolution of hydrogen bromide fumes which were trapped in the tower, and the heat of neutralization was observed in the tower as a result of this reaction. A brown oil was collected in the receiving flask. This oil was redistilled with a loss of more hydrogen bromide and two fractions were collected. Fraction 1,104-107°C.; Fraction 2, 110° - 114°C. under 3 mm. No attempt was made to determine the percentage of bromine in either sample.

The Oxidation of 1-Phenyl-2,3-Dimethyl Butene-1. This mono-olefine (3.96 g.) was mixed with 50 cc. of distilled water in a 300 ml. three-neck round-bottom flask fitted with a mechanical stirrer. To this was added 5.23 grams of potassium permanganate and 16 cc. of freshly distilled pyridine. The mixture was stirred for a period of 30 hours until the color of the permanganate had disappeared. A cooling bath was placed around the flask to keep the temperature of the mixture below 30°C. When the oxidation was completed, an attempt to make the bisulfite addition product of possible low molecular weight carbonyl compounds was made in the

following manner. Sulfur dioxide (from cylinder) was passed through the mixture.* After twenty minutes the reaction flask became very hot and was placed in an ice bath. After ninety minutes a white ppt. began to form in the bottom of the reaction flask. Within another half hour this precipitation began to dissolve, and 1 gram of sodium hydroxide was added to the mixture causing the re-precipitation of a white solid. Finally 3 g. of C. P. sodium bisulfite was added to assure that an excess of $NaHSO_3$ was present in the solution. This white precipitate was filtered and recrystallized several times from 50% aqueous ethyl alcohol. These crystals were dried for several days in the desicator and melted at 119.5°C. Approximately 1.7 grams were reclaimed. When mixed with an authentic sample of benzoic acid the M. P. of these crystals was 119.5-121°C. This compound was therefore benzoic acid, and was one of the fragments of oxidation. A second oxidation of the mono-olefine was carried out under identical experimental conditions, but water alone was used as the solvent. Benzoic acid was obtained in good yields also from this oxidation. Despite repeated attempts the expected methyl-isopropyl ketone was not isolated.

The Addition of Hydrogen Bromide to 1-Phenyl-2,3-Dimethyl Butadiene-1,3. The hydrogen bromide used was prepared by a

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*Use of the sulfur dioxide had a dual purpose. It also removed the manganese dioxide mud formed by the reduction of potassium permanganate.

modification of the method reported by D. R. Duncan,[1] in Inorganic Synthesis. The hydrocarbon, (1-phenyl-2,3-dimethyl-butadiene-1,3), (85.6 g.) was introduced into a reaction flask (40 cm. long and 4.5 cm. in diameter) containing 350 cc. of benzene as the solvent. A steady stream of pure dry hydrogen bromide was bubbled through the solution in the flask for four and one half hours. The flask became warm and the mixture turned green after passing in hydrogen bromide for approximately two hours. The color remained throughout the course of the reaction. The benzene solution was washed free of hydrogen bromide with a dilute solution of sodium carbonate followed by water and dried over calcium chloride. The benzene was then removed by distillation at reduced pressure from the water pump while heating over a water bath. In some instances, the benzene was removed without washing away the excess unreacted hydrogen bromide. The green liquid residue was distilled under reduced pressure. Two large sold lime towers and a cold trap were used in the system between the receiving flask and the vacuum pump. There was abundant evolution of hydrogen bromide fumes which were trapped in the towers, and the heat of neutralization was quite evident as a result of the reaction in the towers. At each attempt at distillation, even under very low pressure (0.5 mm.), the loss of hydrogen bromide was very evident.

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[1] H. S. Booth, "Inorganic Synthesis," McGraw Hill Co., New York, (1939), Vol. I. p. 151.

This is evidence that the hydrobromide formed was a very unstable compound. Finally the hydrobromide was distilled under reduced pressure and three fractions were collected; Fraction 1, 79°-83°/12 mm.; Fraction 2, 86-89°C./2 mm.; Fraction 3, 104-111°C/2 mm. These were pale yellow oils. These oils were analyzed for their bromine content, and the results were much lower that the theoretical value for the hydrobromide adduct of 1-phenyl-2,3-dimethyl butadiene.

CHAPTER V

SUMMARY AND CONCLUSIONS

1. A re-examination of the synthesis of the compound, 1-phenyl-2,3-dimethylbutadiene-1,3 was made. The compound was made by the method of Huggins and McBay and by the method of Kohler. The physical constants and the derivatives of the compound prepared by each of these methods are identical. These results do not check with those reported by Kohler.

2. The conjugated hydrocarbon, 1-pheny-2,3-dimethyl-butadiene-1,3 in the presence of Raney nickel adds hydrogen in the 3-4 position.

3. Hydrogen bromide has been added to the hydrocarbon, and the resulting adduct is extremely unstable. It has not been characterized.

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